

Layer-By-Layer Self-Assembled Multilayer Films of Single-Walled Carbon Nanotubes and Tin Disulfide Nanoparticles with Chitosan for the Fabrication of Biosensors

Yan Pan,^{1,2} Yu-Zhong Zhang,³ Yong Li⁴

¹Analysis and Testing Central Facility of Anhui University of Technology, Maanshan 243000, People's Republic of China

²National Center for Quality Supervision & Testing of Steel Material Products, Maanshan 243000, People's Republic of China

³College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, People's Republic of China

⁴School of Mathematics & Physics, Anhui University of Technology, Maanshan 243000, People's Republic of China

Correspondence to: Y. Li (E-mail: yongli@ahut.edu.cn)

ABSTRACT: In this study, multilayer films containing chitosan, tin disulfide (SnS₂) nanoparticles, and single-walled carbon nanotubes were prepared on glassy carbon electrodes with the use of a layer-by-layer assembly technique. The resulting films were characterized with cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), scanning electron microscopy, and ultraviolet–visible absorption spectroscopy. The results of CV and EIS indicates that the peak currents and charge-transfer resistance all had linear responses to the number of assembled layers. The multilayer-film-modified electrode showed excellent electrocatalytic properties for some species, such as dopamine hydrochloride (DA), ascorbic acid (AA), and uric acid (UA). The well-separated voltammetric signals of DA, UA, and AA could be obtained on the assembled multilayer-film-modified electrode, and the peak-to-peak potential separations were 171, 136, and 307 mV for DA–UA, DA–AA, and UA–AA on CV, respectively. These facts showed that the multilayer-film-modified electrode could be used as a new sensor for the simultaneous detection of DA and UA in the presence of AA in a real sample. In addition, the multilayer films were stable, selective, and reproducible. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: electrochemistry; self-assembly; separation techniques

Received 3 December 2011; accepted 14 June 2012; published online

DOI: 10.1002/app.38216

INTRODUCTION

As a novel nanometer material with unique electrical and mechanical properties, carbon nanotubes (CNTs) have received considerable interest since their discovery.^{1,2} Because of their excellent electrocatalytic activities, such as in promoting the electron-transfer reaction of redox protein and the electrochemical oxidation of nicotinamide adenine dinucleotide hydrogen (NADH), dopamine hydrochloride (DA), ascorbic acid (AA), and epinephrine (NE), CNTs have been widely used for electroanalytical applications.^{3–10} Also, much work on the properties of some electrochemical sensors based on CNTs has been carried out in recent years.¹¹ However, a major barrier to the preparation of CNT-based biosensors is the insolubility of CNTs in most solvents. Generally, CNTs are first dispersed in *N,N*-dimethylformamide or acetone, then cast onto the electrodes, and immobilized through solvent evaporation. The resulting CNT layer is mechanically and electrically loose, and this shortage limits its application in biosensor systems. A combination of

CNTs with other materials to fabricate functional composites is one way to expand the applications of CNTs.¹² For example, the introduction of chitosan (CS), a polysaccharide biopolymer, into CNT-based sensors has been widely studied in recent years.^{13,14} The CNT/CS composite modified electrodes have been proven to be efficient in the detection of various biomolecules. The incorporation of metal nanoparticles into the CNT/CS composites enhance the performances of the modified electrodes.¹⁵

Because of their good chemical stability, low cost, and intriguing electrical and optical properties, tin disulfide (SnS₂) nanoparticles have gained much attention in light-sensitive photocatalysts,¹⁶ solar cells and optoelectronic devices,^{17,18} electrodes for lithium-ion batteries,¹⁹ and gas sensors.²⁰ For example, SnS₂ is used as fabricating glucose electrochemical biosensors because of its small band gap, which is favorable for conducting electrons from biomolecules.²¹ However, the study of SnS₂ as a supporting material for fabricating other biosensors has not been reported.²²

The layer-by-layer (LBL) assembly technique is one of the most successful methods for preparing thin films, and it can control the thickness and structural morphology of a film.²³ This technique is based on the alternating adsorption of oppositely charged materials, and thin films of various proteins and nanoparticles can be prepared via this method.^{24–27} In this study, we assembled functionalized single-walled carbon nanotube (SWNT) and SnS₂ multilayer films on glassy carbon electrodes (GCEs) by alternately assembling positively charged SnS₂, which was dispersed in CS, and negatively charged SWNTs on the basis of electrostatic interaction. The assembled multilayer films were characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), and ultraviolet–visible (UV–vis) absorption spectroscopy. The electrochemical signals of DA, uric acid (UA), and AA were well separated in the multilayer-film-modified electrode, so the multilayer-film-modified electrode could be used as a sensor for the simultaneous determination of DA and UA in the presence of AA.

EXPERIMENTAL

Materials

CV, differential pulse voltammetry (DPV), and alternating-current impedance analysis were performed with a CHI 650C electrochemical workstation (Shanghai, China). A conventional three-electrode configuration was used throughout the experiment. This experiment involved a platinum wire auxiliary electrode, a saturated calomel reference electrode, and a bare or (SWNT/CS–SnS₂)₄-film-modified GC working electrode. All electrolyte solutions were purged for 20 min in high-purity N₂ before the measurement, and a blanket of N₂ was maintained over the solutions during the measurement.

The SEM images were obtained with a JSM-6700F scanning electron microscope (Beijing, China), and UV–vis absorption spectroscopy was obtained with a Cary 500 Scan spectrophotometer (Palo Alto, USA).

SWNTs with carboxylic acid groups were purchased from Time-nano Co. (Chengdu, China) and were used without further purification (purity > 90%). SnS₂ nanoparticles were prepared by the solvent–thermal synthesis method according to a literature procedure.²⁶ CS, DA, AA, and UA were purchased from Sigma (Shanghai, China). The other chemicals were analytical-reagent grade. Phosphate buffered saline (PBS; 0.1 mol/L) solutions with different pH values were prepared by the mixture of stock standard solutions of K₂HPO₄ and KH₂PO₄, and the pH values were adjusted with H₃PO₄ or NaOH. All solutions were prepared with double-distilled water.

SWNTs with carboxylic acid groups (10.0 mg) could be well dispersed in 10.0 mL of *N,N*-dimethylformamide with the aid of ultrasonication to give a 1.0 mg/mL stable black suspension. The CS solution (0.25 wt %) was prepared according to the reported method.²⁷

CS (2.5 mg) was dissolved in 1 mL of 0.05M HCl, and the pH of the solution was adjusted to 5.0 with concentrated NaOH. SnS₂ nanoparticles were dispersed in a 0.25 wt % CS solution with the aid of sonication for 12 h to give a homogeneous yellow suspension.

Assembly of the (SWNT/CS–SnS₂)_n Films

First, the bare GCE with a diameter of 3.0 mm was lightly polished with 0.5- μ m alumina (Shanghai, China) and sonicated in 1 : 1 nitric acid, acetone, and double-distilled water for 10 min, respectively. The electrochemical pretreatment was performed by cycling from a potential -0.2 to $+1.6$ V at a scan rate of 100 mV/s in a 1.0M H₂SO₄ solution. The pretreated electrode was rinsed with water and used for the preparation of the multilayer films.

The general procedure for LBL multilayer preparation is expressed as follows: the pretreated GC electrode was alternately immersed into positively charged CS–SnS₂ and negatively charged SWNTs. The assembly time for each layer was 30 min, and the electrode was well rinsed with double-distilled water after each assembly.

Electrochemical Measurement Procedure

PBS (5.00 mL), containing a suitable amount of special substance, was added to the 10.0 ml voltammetry cell. The solution was purged with nitrogen for 20 min, and the flow of nitrogen over the cell was maintained throughout the experiment. In DPV measurement, potential scanning was made in the range -0.2 to $+0.6$ V. The pulse height was 50 mV, and the scan rate was 5 mV/s. The anodic curves were recorded. The injections were analyzed by the standard addition method. All experiments were conducted at room temperature.

The Faradaic impedance spectra were performed in the presence of a 10 mmol/L K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1 : 1) redox couple. All impedance spectra were measured with an alternating-current modulation of 5 mV over the frequency range from 1 Hz to 100KHz; the applied bias potential was 0.27 V (vs the saturated calomel electrode).

RESULTS AND DISCUSSION

Assembly of the Multilayer Films and SEM Images

In acidic aqueous solution, CS was used as a cationic polyelectrolyte ($pK_a = 6.3$). When SnS₂ nanoparticles were dispersed in the CS solution, the polyelectrolyte CS was wrapped on the surface of the SnS₂ nanoparticles; this resulted in positively charged CS–SnS₂. First, the pretreated GC electrode was immersed into positively charged CS–SnS₂; then, CS–SnS₂/GCE was immersed into a negatively charged SWNT suspension. The growth of the SWNT/CS–SnS₂ composite film after one and four assembly cycle(s), respectively, was directly visualized by SEM. Only nanotubes and a little nano-SnS₂ could be seen in the images because of the invisibility of CS. After one SWNT layer was deposited, the evenly distributed nanotubes only covered a part of the electrode surface [Figure 1(A)]. Subsequently, the (SWNT/CS–SnS₂)₄ composite film composed of tangled SWNTs [Figure 1(B)] showed a uniform morphology, and the electrode surface was almost completely covered. The gradual growth of the films indicated the successful electrostatic LBL assembly of the SWNTs and CS–SnS₂.

UV–vis Absorption Spectroscopy

UV–vis absorption spectroscopy was used to follow the assembly process of the multilayer films growth because the SWNTs showed an absorption peak at 270 nm.²⁸ Figure 2 shows the UV–vis absorption spectra of the (SWCNT/CS–SnS₂)_n multilayer films with layer numbers (*n*'s) of 1, 2, 3, 4, or 5. It could

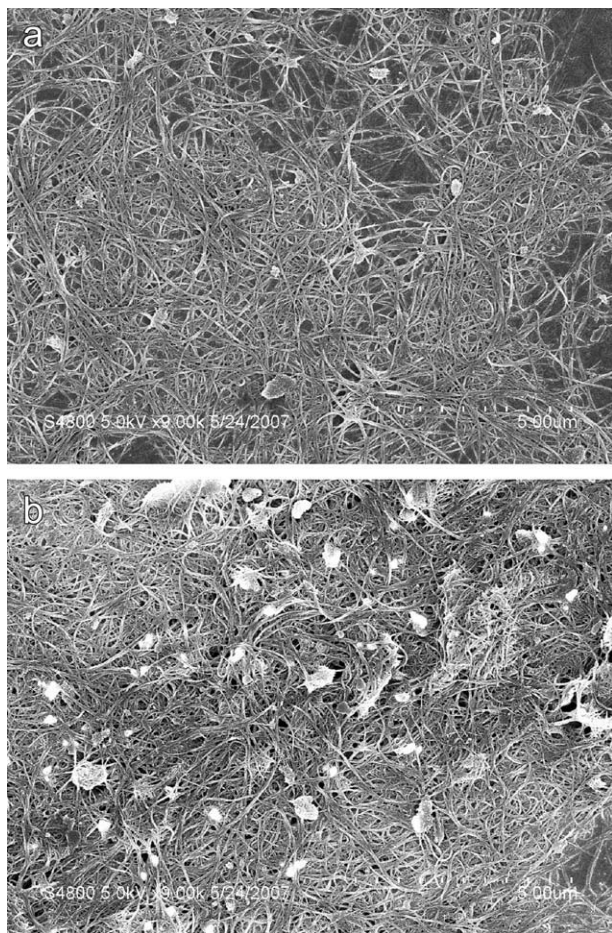


Figure 1. SEM images of (SWNT/CS-SnS₂)_n multilayer films with *n* = (a) 1 and (b) 4.

be seen that the multilayer adsorption of the (SWCNT/CS-SnS₂)_n films was reproducible with sequential deposition. The strong band with a peak at 270 nm almost increased with assembled *n*'s from 1 to 5. This fact suggests that the amount of

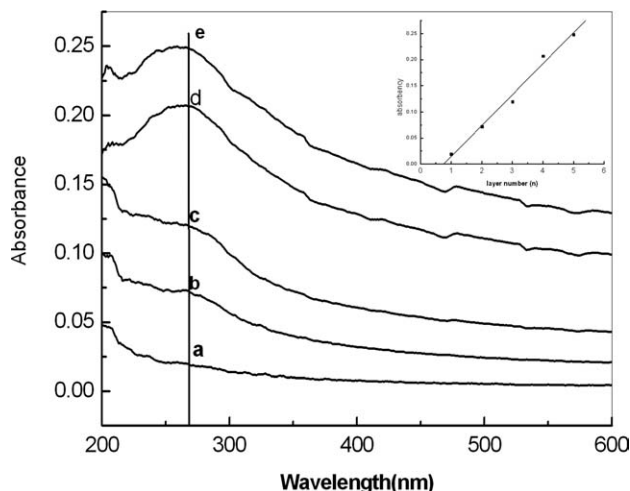


Figure 2. UV-vis absorption spectra of the (SWCNT/CS-SnS₂)_n multilayer films with *n* = 1, 2, 3, 4, and 5.

SWNTs in each assembly step was almost the same, and the assembly of the multilayer films was uniform. Thus, the amount of SWNTs could be simply controlled by the selection of *n*.

Electrochemistry Measurement

EIS provides an effective method for probing the features of the surface-modified electrode. The value of charge-transfer resistance (*R*_{ct}) is usually dependent on the dielectric and insulating features of the electrode/electrolyte interface. Figure 3 shows the Nyquist plots of the impedance spectroscopy in 5 mmol/L Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ (1 : 1) in different film-modified electrodes. It could be seen that the plot of the bare GCE showed the greatest semicircle, which corresponded to the largest *R*_{ct} due to the electrostatic repulsion between the negatively charged surface and the probe molecule Fe(CN)₆^{3-/4-} (curve a). After the adsorption of CS-SnS₂, the surface became positively charged; this resulted in the lowest electron-transfer resistance (curve b). With further adsorption of the SWNTs, the surface turned negatively charged again, and *R*_{ct} was further reduced (curve c). The reduction of the electron-transfer resistance may have been caused by the good conductive capability and larger surface area of the SWNTs. Although its surface charge was negative and it exhibited a certain repulsion role to the probe molecule, the SWNT conductive capability was the major factor that influenced the electron-transfer resistance. The amount of SWNTs increased with the number of SWNT/CS-SnS₂ bilayer films. This led to a further decrease of *R*_{ct}. As shown in the inset of Figure 3, a good linear relationship between *R*_{ct} and *n* was observed from one and four layers. This suggested the same amount of SWNTs increased with *n*.

Electrochemistry Investigation of the (SWNT/CS-SnS₂)_n Films

The multilayer films were also characterized by CV. A typical cyclic voltammogram of 5.0 × 10⁻³ mol/L K₃[Fe(CN)₆] in various layer-film-modified electrodes are shown in Figure 4. Obviously, the peak current of redox increased with the number of multilayer films. Because of the increasing amount of SWNTs and SnS₂ immobilized on the electrode surface, the anodic peak current increased. In the meanwhile, the oxidation current

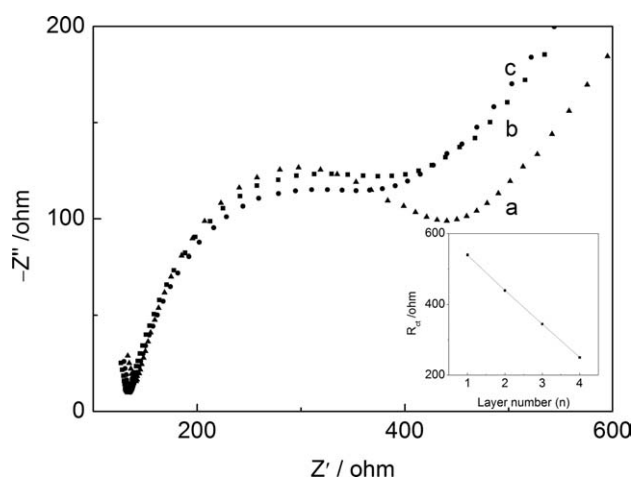


Figure 3. Nyquist plots of the (a) bare electrode, (b) CS-SnS₂/GCE, and (c) (SWNT/CS-SnS₂)₁. Inset: Plot of *R*_{ct} versus *n*.

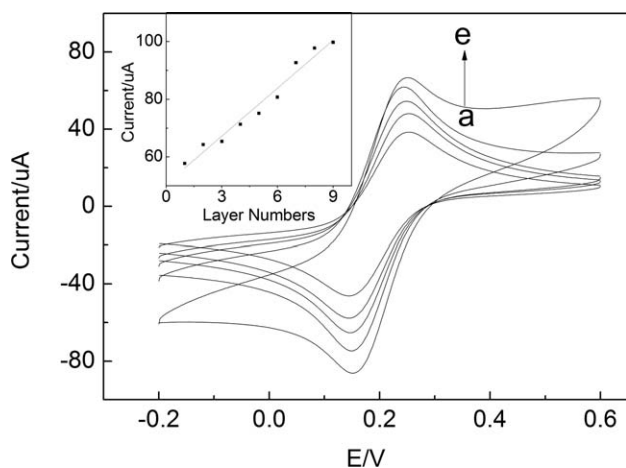


Figure 4. Cyclic voltammograms of 5.0×10^{-3} mol/L $K_3[Fe(CN)_6]$ films with various layers in pH 7.0 PBS containing 0.1 mol/L KCl. The scan rate was 100 mV/s. In the panel, a, b, c, d, and e correspond to $n = 0, 1, 3, 5,$ and $7,$ respectively. E is electric potential. Inset: Plot of the oxidation current versus n .

increased linearly with number of layers (inset in Figure 4); this also suggested that the amount of SWNTs in each assembling step was almost the same.

Electrochemical Activity of DA in Various (SWNT/CS-SnS₂)_n-Film-Modified Electrodes

DA is a neurotransmitter, and it has two hydroxyl groups to that are easily oxidized. DA was selected as the redox probe for investigating the electrochemical activity of the assembled membrane-modified electrode because it can be observed as a pair of redox peaks in CV in most electrodes. The anodic current of 2.0×10^{-5} mol/L DA as a function of the n value of the modified electrode films is shown in Figure 5. The highest anodic current was observed in the four-layer film. The current began to decrease with further increases in the number of layers. Therefore, the four-layer film showed the optimum response to DA. It should be noted that the increase in the n values could bring about a positive effect as well as a negative one. First,

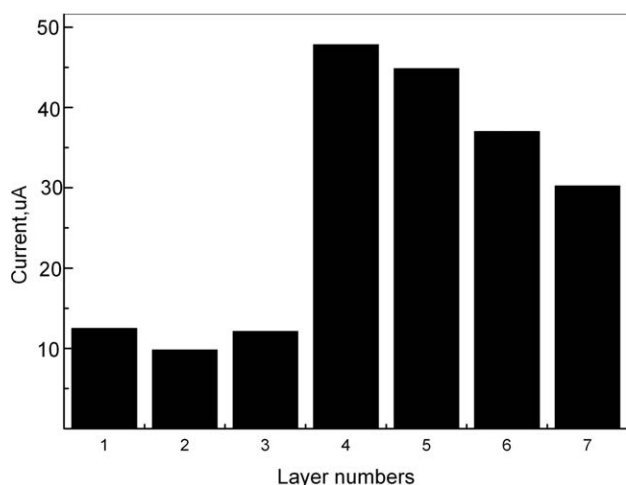


Figure 5. Effect of the film layers (n 's) on the oxidation current of 2×10^{-5} mol/L DA in 0.1 mol/L PBS at pH 7.0.

with increasing n values, the quantity of nanoparticles accumulated gradually, and the film thickness increases. The increase in the number of nanoparticles on the modified electrode increased the electrode surface area and sped up electron transfer. This effect resulted in an enhancement of the current. The second effect was that increase in the film thickness created a barrier for electronic transference. As shown in Figure 5, the current reached a maximum with an n value of 4. With further increasing n values, the second effect was enhanced gradually, and the current dropped slowly. The effect of the solution pH value on the response to DA was investigated in the range 2.0–9.0, as shown in Figure 6. The results show that the anodic peak current of DA increased with solution pH and reached its maximum when the pH was 7.0 and then decreased when the pH was greater than 7.0. In the meanwhile, the anodic peak potentials of the oxidation of DA shifted negatively with an increase in pH; this indicated that protons took part in the DA reaction processes, so a pH value of 7.0 was selected as the optimum pH value. Because the (SWNT/CS-SnS₂)₄-film-modified electrodes had the best electrochemical response to DA, the (SWNT/CS-SnS₂)₄ film was selected for the sensing layer in the following experiments.

Electrochemical Oxidation of DA, AA, and UA in the (SWNT/CS-SnS₂)₄-Film-Modified Electrodes

Practical applications of the proposed electrode were tested by three biological compounds, DA, UA, and AA. It is well known that they coexist in the extracellular fluid of the central nervous system and serum, and they have similar oxidation potentials on a bare electrode, so it is very important to distinguish their electrosignals. The selectivity and sensitivity of the three biological compounds discussed previously could be improved with this modified electrode. CV and DPV were used to investigate the electrochemical activity.

The electrochemical oxidation of DA, AA, and UA in various electrodes is shown in Figure 7. An overlapped anodic peak was observed in the bare GCE [curve a in Figure 7(A)], and the electrochemical signals of DA, AA and UA were indistinguishable in the bare GCE. In the (SWNT/CS)₄-film-modified electrode, three well-defined oxidation peaks were observed, but the

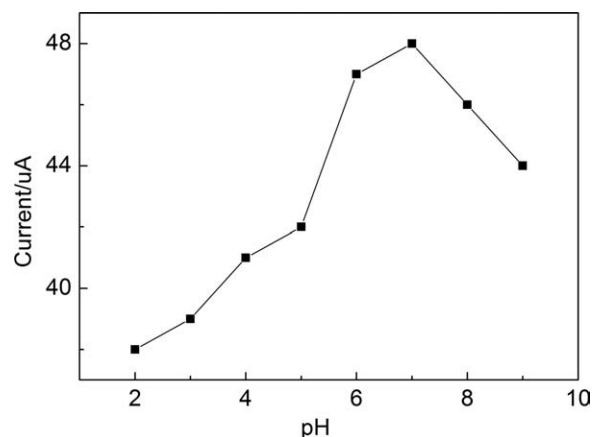


Figure 6. Effects of the solution pH value on the anodic current response of 2.0×10^{-5} mol/L DA.

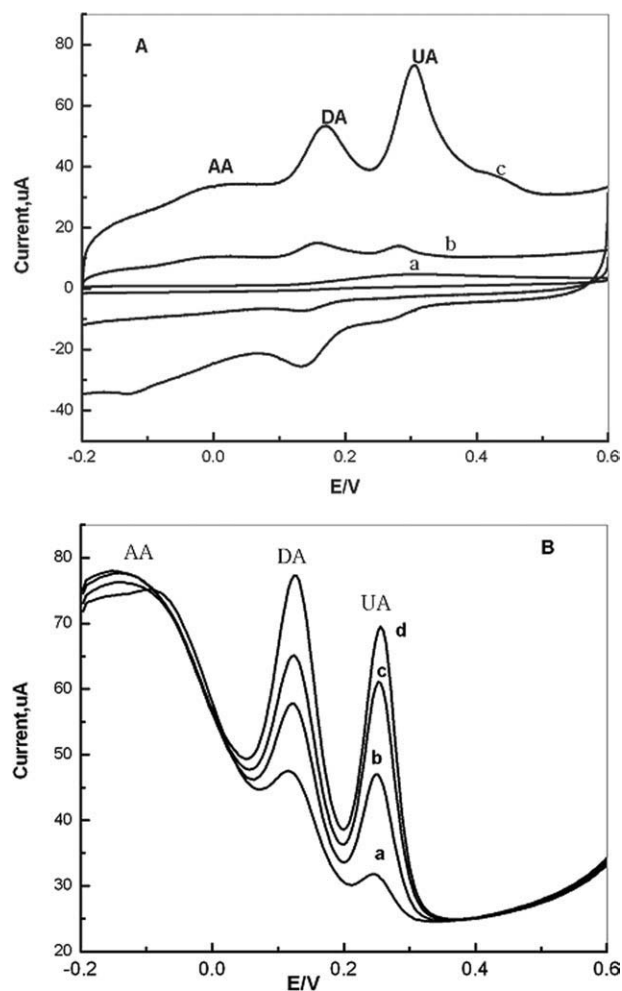


Figure 7. (A) Cyclic voltammograms of 1.0×10^{-5} mol/L DA + 1.0×10^{-4} mol/L AA + 2×10^{-5} mol/L UA in PBS at pH 7.0 (a) in the bare GC electrode, (b) in the (SWCNT/CS)₄ modified GC electrode, and (c) in the (SWCNT/CS–SnS₂)₄ modified GC electrode. The scan rate was 100 mV/s. (B) DPV voltammograms of DA and UA in the (SWNT/CS–SnS₂)₄-film-modified electrode in 0.1M PBS of pH 7.0 containing 2×10^{-4} mol/L AA, DA concentrations = 1, 5, 10, and 15 μ mol/L and UA concentrations (a–d) of 1, 5, 10, and 15 μ mol/L, respectively. E is electric potential.

peak currents were small [curve b in Figure 7(A)]. In the (SWNT/CS–SnS₂)₄-modified electrode [curve c in Figure 7(A)], the electrochemical signal of the three compounds were well distinguished, and the peak currents were distinctly enhanced. Obviously, the peak separations were 171, 136, and 307 mV for DA–AA, DA–UA, and UA–AA, respectively. This fact shows that it was possible to simultaneously determine DA and UA or to detect DA in the presence of AA and UA with the (SWNT/CS–SnS₂)₄-film-modified electrode.

DPV was used to estimate the linear range of DA and UA. Figure 7(B) shows the DPV recordings at various DA and UA concentrations in the (SWNT/CS–SnS₂)₄-film-modified electrode in the presence of 1.0×10^{-4} mol/L AA. It was found that the DPV peaks for AA, DA, and UA oxidation in the assembled modified film were clearly separated from each other when they coexisted in pH 7.0 PBS, and the peak heights of DA and UA also increased

with the DA and UA concentrations, respectively. Thus, AA had no influence on the determination of the DA and UA concentrations. The anodic peak current (*i*_{pa}) of DA increased linearly with its concentration (C) from 1.0×10^{-6} to 5.0×10^{-5} mol/L; the linear regression equation was as follows:

$$i_{pa}(\mu A) = 3.37 + 0.126C(\mu mol/L)$$

with a correlation coefficient of 0.9960 and a detection limit of 7.0×10^{-7} mol/L (Signal-to-noise ratio is 3). Similarly, the peak current of UA was linear with concentrations from 2.0×10^{-6} to 4.0×10^{-5} mol/L. The linear regression equation was

$$i_{pa}(\mu A) = 1.03 + 0.184C(\mu mol/L)$$

with a correlation coefficient of 0.9920.

It should be noted that interference from some other substances was investigated. For example, no interference from the following compounds, NaCl (400 μ mol/L), MgCl₂ (300 μ mol/L), CaCl₂ (300 μ mol/L), citric acid (100 μ mol/L), glucose (100 μ mol/L), or cysteine (100 μ mol/L), was observed for 10 μ mol/L DA and 10 μ mol/L UA.

Stability and Reproducibility of the Multilayer Films

The stability of the multilayer films was investigated by CV. The peak current of DA hardly changed when the modified electrode was stored in air or in 0.1 mol/L pH 7.0 PBS for at least 2 weeks. This indicated that the multilayer film was stable and did not suffer from surface fouling by the oxidation products of voltammetric measurements.

The reproducibility of the multilayer film was also investigated. The relative standard deviation of five successive scans was 2.0% for 1.0×10^{-5} mol/L DA; this indicated excellent reproducibility in the modified electrode.

Determination of DA in the Real Samples

DA injection was used to evaluate the test capability, such as the selectivity and reproducibility, of the multilayer-film-modified electrode. The determination results are listed in Table I. They were in accordance with the results by the China Pharmacopoeia method²⁹ and showed that the proposed methods could be efficiently used for the determination of DA in injections.

Stability of the Modified Electrodes

The stability of a modified electrode is an essential issue in practical applications; however, the Langmuir–Blodgett (LB) multilayer casting film and even some self-assembled

Table I. Determination Results of DA in the DA Injections

Sample	Label (mg/mL)	Found (mg/mL)	Relative Standard Deviation (%)	Recovery (%)	Pharmacopoeia method (mg/mL)
1	2.0	1.99	2.1	99.5	2.01
2	2.0	2.01	2.2	100.5	2.02
3	2.0	2.03	2.4	101.5	2.05

n = 8.

monolayer modified electrodes show poor stability in electrolyte solution. The CV curves of the SWNT multilayer-film-modified electrodes after 1 and 300 circles were measured. The results show no significant difference between the two cases for CV. This indicated that the modified electrode had good stability.

CONCLUSIONS

We assembled (SWNT/CS-SnS₂)₄ multilayer films on GCE by the LBL technique. The assembled multilayer film was investigated by CV, EIS, SEM, and UV-vis absorption spectroscopy. The application of the (SWNT/CS-SnS₂)₄-film-modified electrodes were investigated with neurotransmitters. The electrochemical signals of DA, UA, and AA were well separated in the assembled multilayer-film-modified electrode, so AA interference was repelled. The method could be applied to the detection of DA and UA in the presence of AA.

ACKNOWLEDGMENTS

This project was supported by the National Nature Science Foundation of China (No. 20675002), the Key Nature Science Foundation of Anhui Province Ministry of Education (No. 2006Kj 040A), and Foundation of Outstanding Yong Talent in University of Anhui Province (No. 2010SQRL042).

REFERENCES

1. Iijima, S. *Nature* **1991**, *56*, 354.
2. Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787.
3. Luo, H.; Shi, Z.; Li, N.; Gu, Z.; Zhuang, Q. *Anal. Chem.* **2001**, *73*, 915.
4. Gong, K.; Zhang, M.; Yan, Y. *Anal. Chem.* **2004**, *76*, 6500.
5. Yang, P.; Zhao, Q.; Gu, Z.; Zhuang, Q. *Electroanalysis* **2004**, *16*, 97.
6. Davis, J.; Coles, R.; Hill, H. A. O. *J. Electroanal. Chem.* **1997**, *440*, 279.
7. Zhang, Y.; Cai, Y.; Su, S. *Anal. Biochem.* **2006**, *350*, 285.
8. Wang, J.; Li, M.; Shi, Z.; Li, N.; Gu, Z. *Electroanalysis* **2002**, *14*, 225.
9. Zhang, P.; Wu, F.; Zhao, G.; Wei, X. *Bioelectrochemistry* **2005**, *67*, 109.
10. Wang, Z.; Liang, Q.; Wang, Y.; Luo, G. *J. Electroanal. Chem.* **2003**, *540*, 129.
11. Zhao, Q.; Gan, Z.; Zhuang, Q. *Electroanalysis* **2002**, *14*, 1609.
12. Baughman, R.; Zakhidov, A. *Science* **2002**, *297*, 787.
13. Liu, A.; Honma, I.; Zhou, H. *Biosens Bioelectron* **2005**, *21*, 809.
14. Tan, X.; Li, M.; Cai, P. *Anal. Biochem.* **2005**, *337*, 111.
15. Lin, J.; He, C.; Zhao, Y. *Sens Actuators B* **2009**, *137*, 768.
16. Yang, C.; Wang, W.; Shan, Z. *J. Solid State Chem.* **2009**, *182*, 807.
17. Deshpande, N.; Sagade, A.; Gudage, Y. *J. Alloys Compd.* **2007**, *436*, 421.
18. Panda, S.; Antonakos, A. *Mater. Res. Bull.* **2007**, *42*, 576.
19. Kim, T.; Kim, C.; Son, D. *J. Power Sources* **2007**, *167*, 529.
20. Shi, W.; Huo, L.; Wang, H. *Nanotechnology* **2006**, *17*, 2918.
21. Kang, X.; Wang, J. *Biosens Bioelectron* **2009**, *25*, 901.
22. Yang, Z.; Hu, X. *Biosens Bioelectron* **2011**, *26*, 4337.
23. Zheng, L.; Yao, X.; Li, J. *Curr. Anal. Chem.* **2006**, *2*, 279.
24. Zhou, Y.; Li, Z.; Hu, N.; Zeng, Y. *Langmuir* **2002**, *18*, 8573.
25. Sun, H.; Hu, N. *The Analyst* **2005**, *130*, 76.
26. Wang, X.; Huang, H.; Liu, A.; Liu, B. *Carbon* **2006**, *44*, 2115.
27. Zhang, M.; Gong, K.; Zhang, H.; Mao, L. *Biosens Bioelectron* **2005**, *20*, 1270.
28. Rouse, J.; Lillehei, P.; Siochi, E. *J. Chem. Mater.* **2004**, *16*, 3904.
29. Pharmacopoeia Committee of the Ministry of Health of People's Republic of China. *Pharmacopoeia of People's Republic of China*; Chemical Industry Press: Beijing, **2000**; Chapter 2.